

(Translation)

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**Application Number: Patent Application No. 2001-23038**

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**Applicant(s): LG CHEMICAL Ltd.**

**COMMISSIONER**

I, the undersigned, who have prepared English translation which is attached herewith, hereby declare that the aforementioned translation is true and correct translation of officially certified copy of the Korean Patent Application No. 2001-23038 filed on April 27, 2001

This 3<sup>th</sup> day of March, 2005

Translator:

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## DOUBLE-SPIRO ORGANIC COMPOUNDS

### Description

#### Technical Field

5 The present invention generally relates to a double-spiro type of organic compound, more particularly, to a double spiro type of organic compound which has high melting point and high quantum efficiency, and can control mobility of carrier. The double spiro compound has structure improving hole-transporting, light-emitting, fluorescent dye, and electron-transporting properties.

10

#### Background Art

15 Organic EL is a device emitting light by forming thin layer comprising organic material between two electrodes(a cathode and an anode), receiving and transporting a hole and an electron injected from each electrode and recombining a hole and an electron injected. Durability and efficiency of organic EL can be improved by election of electrodes and organic material used. And when device is manufactured, display of full color can be manufactured by forming red pixel, green pixel and blue pixel using shadow mask.

20 Performance of the organic EL was improved by forming thin layer using organic material having double-layer structure, disclosed in USP 4,359,507. Recently, efficacious organic EL was prepared by using four layers structure comprising a hole injecting layer which can receive a hole from an anode, a hole transporting layer which can transport a hole, an emitting layer which can emit a light by combining a hole and an electron, and an electron transporting layer which 25 can transport an electron from a cathode to an emitting layer. Organic compounds forming each layer have to have stability to an electron or a hole. When forming thin layer, general requirement is to form non-crystal and uniform layers. And, organic EL is stable to heat generated by driving or high temperature of the outside.

30 The thermal stability is superior as glass transition temperature of material used is higher. Otherwise, if molecular weight is increased to raise glass transition temperature, vapor deposition is generally difficult. Therefore, it is important to maintain sublimability of material in need of vapor deposition as well as to raise glass transition temperature.

35 General method used for achieving the above object is to introduce aromatic group or heterocyclic group to material used. If number of saturated hydrocarbon

not aromatic hydrocarbon is increased, sublimability is relatively decreased. However, aromatic group having flat structure introduced into molecule accelerates overlap of pi-orbital between molecules, and inhibits performance of organic EL such as trap inhibiting carrier transport, quenching site inhibiting efficiency of emission, and formation of excimer by interacting between molecular orbitals in ground state.

Generally used materials have various chemical structures according to their function. A hole injecting material uses compound having thermal stability and maintaining stable interface with an anode. For example, USP 4,356,429 discloses copper phthalocyanine(CuPc) which is developed by Kodak co. in US. Aryl amines which have variously substituted with aromatic ring from center of nitrogen atom are most typical material of a hole transporting material. The aryl amines have generally been used since a hole transporting rate is high and electronic stability to a hole is excellent. To improve thermal stability of the aryl amines, a large number of aryl amines may be introduced into one molecule or naphthyl substituent instead of phenyl substituent may be introduced(USP 5,554,450). The model example is 4,4'-bis-[N-(1-naphthyl)-N-phenyl-amino]biphenyl(NPB). Recently, USP 5,840,217 disclosed a hole transporting material which is spiro type compound substituted with aryl amines and has high glass transition temperature.

A material comprising an emitting layer which emits light by combining a hole with an electron generally uses 8-hydroxyquinoline aluminum salt(Alq3) which emits green fluorescence since it is most stable and has high melting point.

As manufacture of display device having natural color is spotlighted, study on blue fluorescent material becomes active. Blue luminescent body has problem melting point is lower and durability is shorter than Alq3 which is a green luminescent body. The typical blue luminescent body is aromatic hydrocarbon disclosed in USP 5,516,577 and USP 5,366,811. The aromatic hydrocarbon has become known as fluorescence for a long time and is generally used as fluorescent brightener in industry.

To apply adequately to organic EL, a blue luminescent body containing the aromatic hydrocarbon has to have high glass transition temperature and sublimability at the same time for thin layer deposition. Recently, USP 5,840,217 disclosed a blue luminescent body having spiro type improved thermal stability. The spiro type compound which has two pentagonal centers introduces various

substituents into two biphenyls which cross at right angles and forms a blue luminescent body.

USP 5,150,006 and USP 5,645,948 disclosed organic metal compound containing aluminum, heterocyclic organic compound using imidazole group, 5 organic compound containing fused aromatic group.

To improve efficiency of organic EL, USP 4,769,292 discloses that a hole and an electron transported to an emitting layer combines with a fluorescent dye by doping a small dose of the fluorescent dye into an emitting layer or energy transfer occurs from exciton combined at materials comprising an emitting layer to a 10 fluorescent dye. Energy band gap of the fluorescent dye is similar or smaller than energy band gap of material hosting fluorescent dye. Emission corresponding to band gap of fluorescent dye can be obtained according to selection of host material and fluorescent dye, and concentration of fluorescent dye.

When concentration of fluorescent dye is too deep, excimer is formed by 15 overlapping molecular orbital between dyes, and thus efficiency of emission becomes rapidly low or wavelength of emission moves. This is because molecular structure of general fluorescent dye is flat structure consisting of frame of pi-orbital. The example is perylene and anthracene which are blue luminescent dye; quinaridone, coumarine and derivatives thereof which are green fluorescent dye; 20 rubrene which is yellow fluorescent dye, Nile red, DCM and derivatives thereof which are red fluorescent dye.

An electron transporting material which delivers electron from a cathode to an emitting layer has to form stable interface with material comprising electrode at high speed. Like other materials comprising organic EL, an electron transporting 25 material is stable to heat generated when driving device or keeping device and thus has to have high glass transition temperature. And an electron transport material has electronically stability to an electron as well as good temperature of electron. Therefore, green luminescent material, Alq<sub>3</sub> is generally used as an electron transporting material.

30

### Disclosure

#### Technical Problem

One aspect of the present invention provides new organic compound which has high efficiency of proton and control mobility of carrier.

Another aspect of the present invention provides organic compound which 35 uses as organic material such as a hole transporting material, an emitting material, a

fluorescent material, an electron transporting material, or improves efficiency of each organic material.

Another aspect of the present invention provides organic compound having chemical structure which is thermally stable, easily introduce functional group, and minimize overlapping between molecules.

Another aspect of the present invention provides organic compound having high melting point and sublimability required for deposition process.

Another aspect of the present invention provides organic compound having high proton efficiency required for emitting material or fluorescent dye.

Another aspect of the present invention provides organic compound improving durability of device and color of full color display, especially blue color.

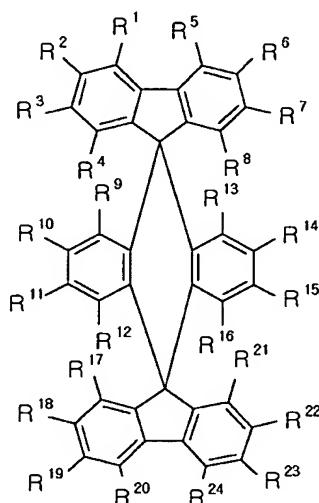
Another aspect of the present invention provides organic compound synthesizing various its derivatives and thus controlling change of emitting wavelength or desirable electronic property.

Another aspect of the present invention provides organic compound used as device required high proton efficiency, device required transporting an electron or a hole, solar cell comprising organic material, optical photo conductor drum used in copier or laser printer, or organic transistor.

#### Technical Solution

To achieve the above objects, the present invention provides double spiro type compound represented by the chemical formula 1 below.

[Chemical Formula 1]



wherein each of R1-R24 is, independently or simultaneously, hydrogen; a halogen group selected from the group consisting of fluorine(F), chlorine(Cl),

bromine(Br), and iodine(I); an aliphatic hydrocarbon of C1-C20, alkoxy group, arylamine group; aromatic hydrocarbon; nitrile(-CN); acetylene group; a heterocyclic compound selected from the group consisting of thiazole, oxazole, imidazole, and thiophene; or a substituent which is moiety of compound represented by formula 1, which are unsubstituted or substituted with at least one of substituent X defined as follows,

5 R10 and 11, and R14 and R15 are independently or simultaneously combined to aromatic ring or heterocycle,

10 the substituent X is hydrogen, halogen group of fluorine, chlorine, bromine, or iodine; aliphatic hydrocarbon of C1-C20, alkoxy group, arylamine group; aromatic hydrocarbon; nitrile(-CN); acetylene group; heterocyclic compound selected from the group consisting of thiazole, oxazole, imidazole, and thiophene; or a substituent which is moiety of compound represented by formula 1, which are unsubstituted or substituted with at least one of substituent X.

15 The present invention will be discussed in more detail as follows.

First, the present invention will be discussed organic EL using double spiro type compound represented by the above chemical formula 1.

Figure 1 showed simple figure of organic EL according to the present invention.

20 In figure 1, the layer 1 is the substrate which supports an anode layer 2. For example, glass, plastic, non-conductive material, ceramic can be used as the substrate. To use conductive material as layer 1, electronic insulating materials have to be used between the layer 1 and the anode layer 2 having conductivity.

25 The anode layer 2 is electronically short-circuited with the cathode layer 3 by organic material. The anode material can use transparent electrode such as indium tin oxide, indium zinc oxide, tin oxide, fluorinated tin oxide. When light produced in organic EL does not need to pass through the layer 1, metal electrode can be used as the anode material. However, all the electrodes require a relatively large work function. When forward bias drives organic EL using electrode having 30 relatively large work function as the anode, a hole injection smooths from the anode to a hole transporting layer 4.

35 The layer 4 which forms interface with anode layer 2 is a hole transporting layer which transports a hole from anode to cathode. An electron transporting layer 5 located between a hole transporting layer 4 and a cathode layer 3 transports an electron from a cathode to an anode. Recombination place between an electron and

a hole can be selected from layers 4 and 5 according to kinds of a hole transporting layer and an electron transporting layer used.

5 A material comprising a cathode layer 3 selects among materials having a relatively small work function such as Al, Mg, Ag, Ca and Li. A cathode layer 3 may also be made of double layers of materials such as magnesium-silver alloy, lithium-aluminum alloy, LiF/Al and Li<sub>2</sub>O/Al. When forward bias drives organic EL using electrode having relatively small work function as the cathode, an electron injection smooths from the cathode to an electron transporting layer 5.

10 Organic EL of figure 2 is similar to that of figure 1, but subdivides organic material layer between layers 2 and 3.

Layers 1 to 3 of figure 2 is respectively substrate, anode, cathode in the same manner as figure 1 and layers 6, 4, 7 and 5 is respectively a hole injecting layer, a hole transporting layer, an emitting layer and an electron transporting layer.

15 To improve brightness, driving voltage and durability, organic EL can further include a hole injecting layer or an emitting layer as shown in figure 2.

20 In figure 2, a hole injecting layer 6 which forms interface with an anode layer 2 forms stable interface with anode material selected from inorganic oxide, metal or conductive polymer, and smooths a hole injection from an anode and thus transports a hole to a hole transporting layer. An emitting layer 7 located between a hole transporting layer 4 and an electron transporting layer 5 recombines with a hole injected from an anode and an electron injected from a cathode so as to emit light and comprises material having high proton efficiency.

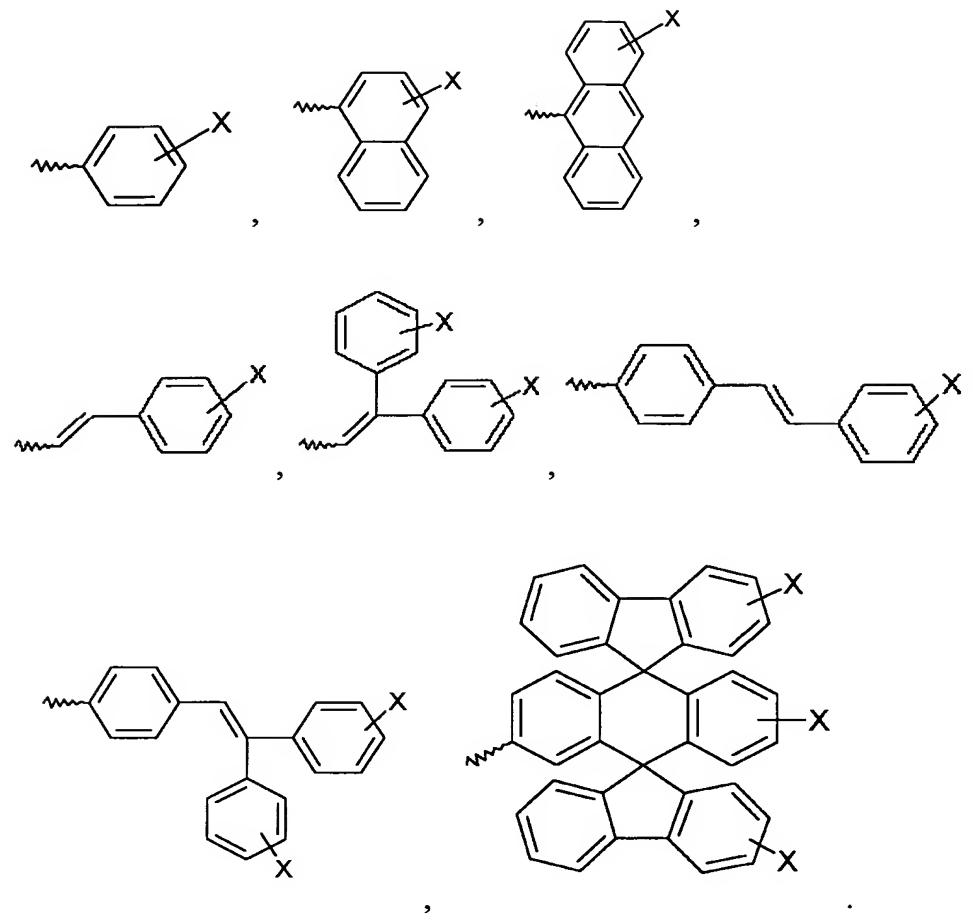
25 To improve performance of organic EL, organic layer between two electrons can be further subdivided besides structure of figures 1 and 2.

Organic material located between two electrodes of organic EL of figures 1 and 2 can independently or simultaneously use compound represented by chemical formula 1.

30 Double spiro type compound of chemical formula 1 will be explained in more detail.

Compound represented by chemical formula 1 wherein R1-R24 are all hydrogen is well-known compound synthesized to study hydration reaction of aromatic carbinol(J. Am. Chem. Soc., 52, 2881, 1930). Compounds provided in the present invention are compounds which introduce various substituents into a frame of well-known double spiro type, and the compound can improve thermal stability, emitting efficiency and durability of organic EL.

The major examples of aromatic hydrocarbon which are substituents of R1-R24 are follows.



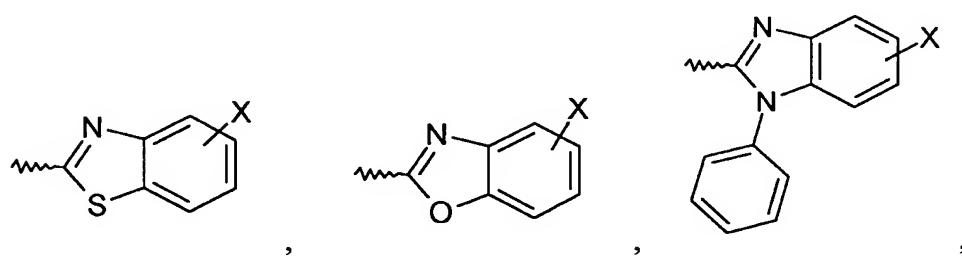
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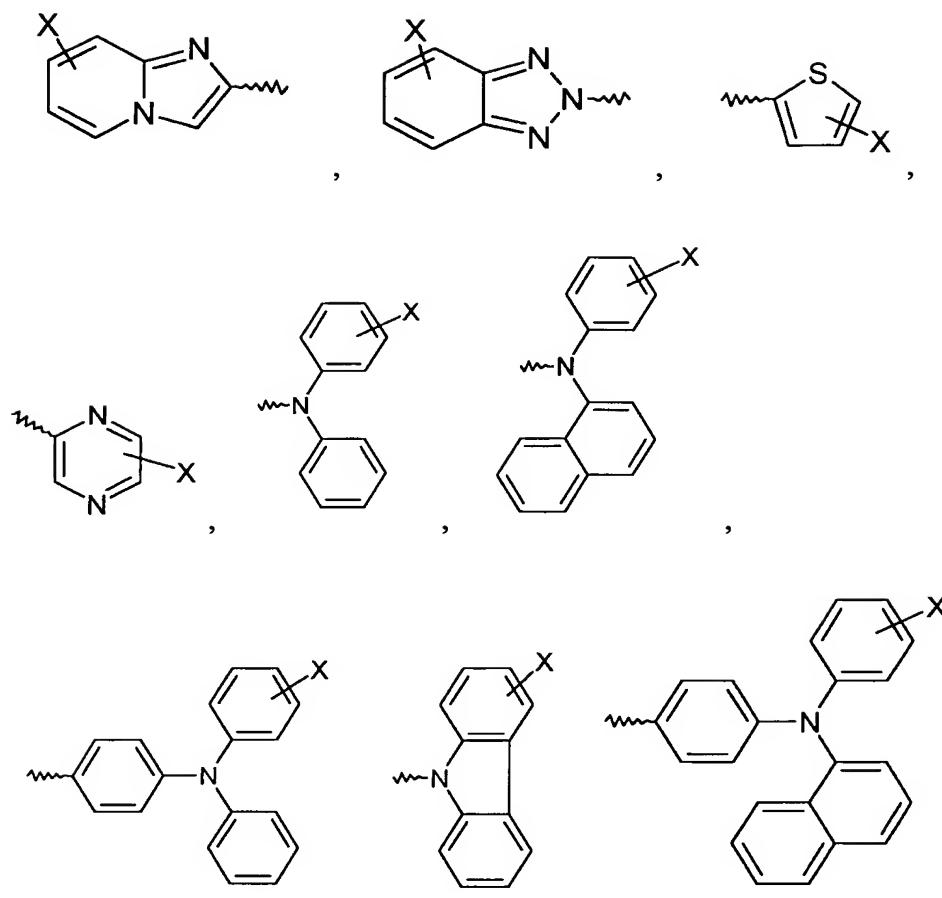
10

Substituents of aromatic hydrocarbon can have sub-substituents represented by one more X. For example, the sub-substituents can be selected from the groups consisting of hydrogen; C1-C20 aliphatic hydrocarbon; halogen such as fluoride, chloride, bromide, iodide; alkoxy; arylamine; aromatic hydrocarbon; heterocyclic compound such as thiazole, oxazole, imidazole; nitrile; acetylene; and moiety of compound of chemical formula 1. And the sub-substituents can form fused ring to be fused with heterocyclic ring of original substituents.

The followings are major examples of heterocyclic compound and arylamine which are substituents of R1-R24.

15

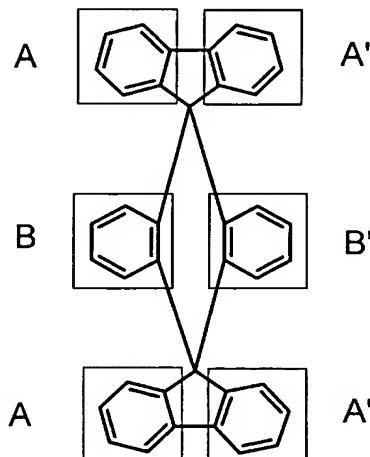




5 The heterocyclic substituents can further comprise sub-stituents represented by one more X which is for example the same as sub-substituents of aromatic hydrocarbon.

Structural property of organic compound which can be applied to organic EL will be explained from chemical formula 1a below.

[Chemical Formula 1a]



Organic EL requires high driving voltage when R1-R24 of chemical formula 1 are all hydrogen or phenyls consisting of A, A', B and B' in chemical formula 1 are all substituted with hydrogen. To lower driving voltage, raise emitting efficiency, or provide a hole transporting ability or an electron transporting ability, carbons of phenyls represented by A, A', B and B' need to be substituted respectively.

5

A plane of phenyls consisting of A and A' and a plane of phenyls consisting of B and B' cross at right angles in space, and phenyls consisting of A and A' occupy approximately twice space than phenyls consisting of B and B' in volume. This property minimizes formation of excimer by overlapping molecular orbitals.

10

Overlapping molecular orbital between emitting molecules located in B and B' can be minimized by electing adequate substituents consisting of A and A', and introducing substituents having emitting property into B and B'.

15

To prevent overlapping molecular orbital, alkyl group(C1-C20) can be introduced into A and A' or functional group which can minimize overlapping molecules can be introduced at other space phase. If overlapping molecules does not form excimer, phenyls of A and A' can also introduce substituents having emitting property.

20

To provide a hole transporting property in compound of chemical formula 1, phenyls of A , A', B or B' can introduce substituents having a hole transporting ability such as arylamine.

25

Other method for improving emitting efficiency of organic EL is to optimize concentration equilibrium of a hole and an electron in organic EL. An excess of carrier do not contribute to emission so as to cause deterioration of proton emitting efficiency and shortening of durability of organic EL. Optimization of carrier concentration is determined by election of electrodes, oxidative level and reductive level of organic material existing between electrodes, and carrier mobility. Recombination place of carriers can be a factor determining durability of organic EL.

30

Therefore, structural change of used organic material requires in manufacturing organic EL efficiently and stably. This object can be achieved by compound of chemical formula 1.

The structure of chemical formula 1a can introduce into phenyls of A, A', B and B' substituents which can highen or lower mobility of an electron or a hole so as to obtain desirable property, and simultaneously introduce functional group controlling mobility of carrier and functional group emitting.

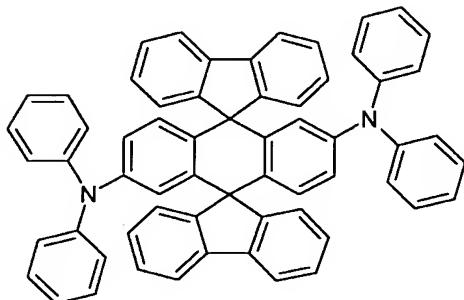
Another method for improving emitting efficiency and durability of organic EL is doping a small quantity of fluorescent dye into emitting layer. Fluorescent dye used in doping is material having similar or smaller energy band gap than material comprising emitting layer.

5 An electron and a hole which are recombined at emitting layer move to fluorescent dye which has low energy band gap in order to emit light. When concentration of fluorescent dye is high, the fluorescent dye forms excimer to reduce proton efficiency.

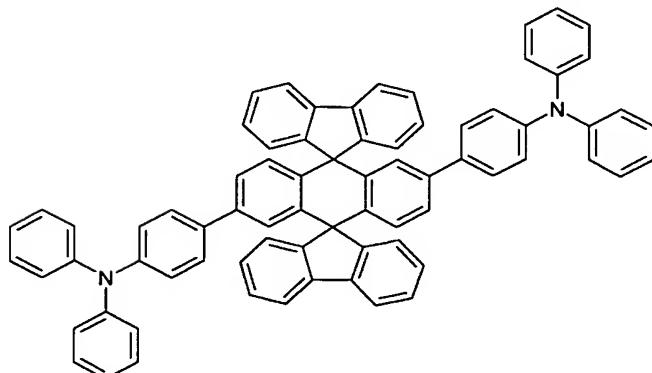
10 Compound of chemical formula 1 according to the present invention can solve the above problems. Emitting group which has relatively low energy band gap is introduced into phenyls of B and B', and functional group which has relatively high energy band gap is introduced into phenyls of A and A'. Therefore, recombination place can be limited to location comprising phenyls of B and B'.

15 Examples introducing into phenyls of B and B' functional group having a hole transporting ability or emitting ability is the following compound of chemical formula 2 to 14.

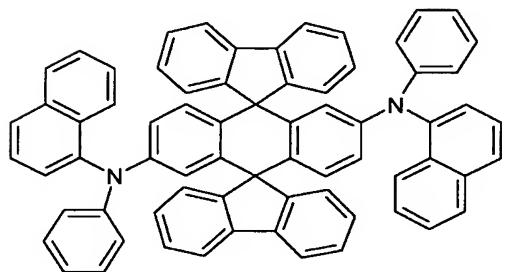
[Chemical Formula 2]



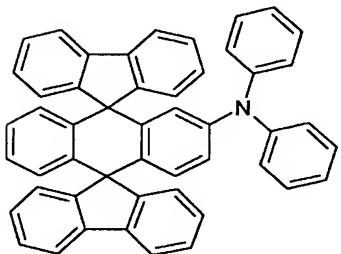
[Chemical Formula 3]



[Chemical Formula 4]

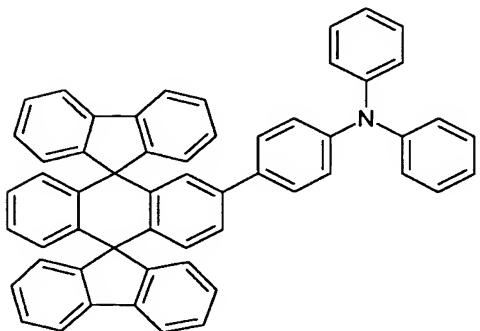


[Chemical Formula 5]

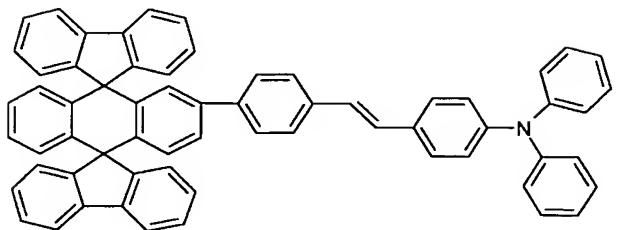


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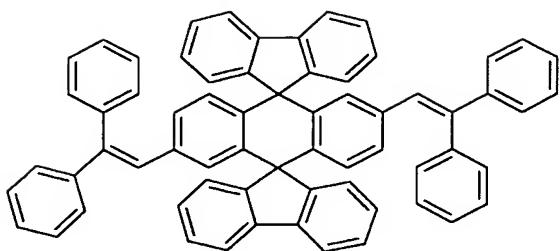
[Chemical Formula 6]



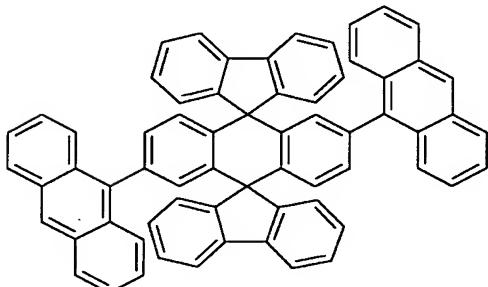
[Chemical Formula 7]



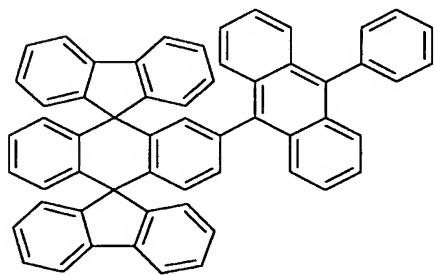
[Chemical Formula 8]



[Chemical Formula 9]

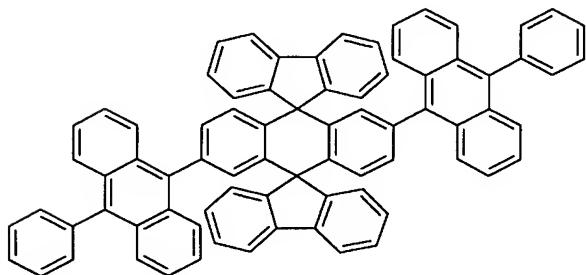


[Chemical Formula 10]

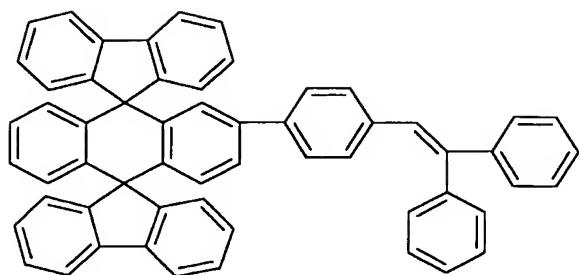


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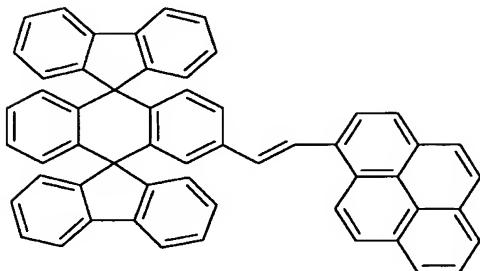
[Chemical Formula 11]



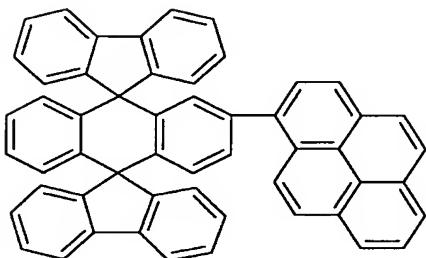
[Chemical Formula 12]



[Chemical Formula 13]



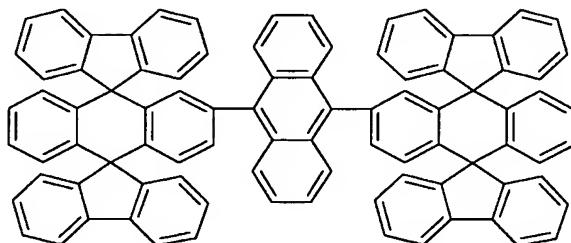
[Chemical Formula 14]



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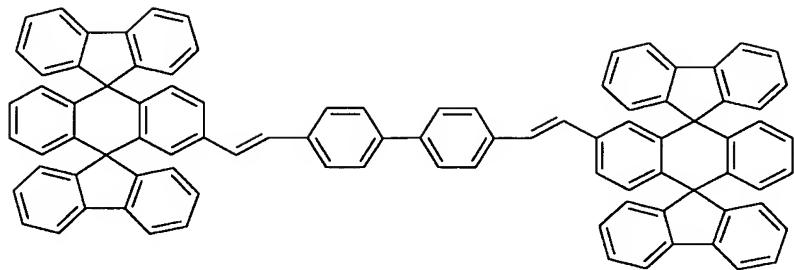
Compound of chemical formula 1 can introduce two more double spiro structures in one molecule and the examples is the following compounds 15 and 16.

[Chemical Formula 15]



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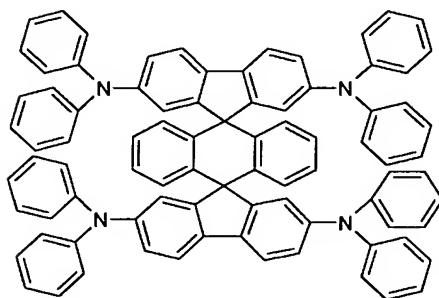
[Chemical Formula 16]



5 Compound of chemical formula 1 can introduce into phenyls of A and A' functional group so as to improve a hole transporting property or an electron transporting property, alkyl group so as to minimize overlapping pi-orbital between molecules in space phase, and emitting group so as to use as material forming an emitting layer.

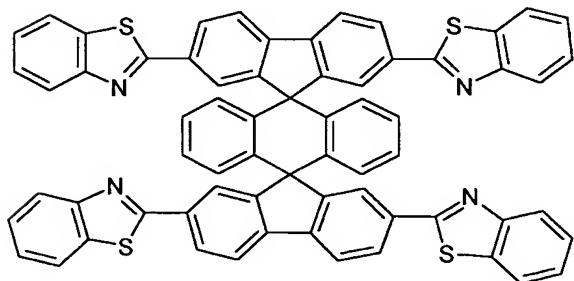
The examples are compound of the following chemical formula 17 to 22.

[Chemical Formula 17]

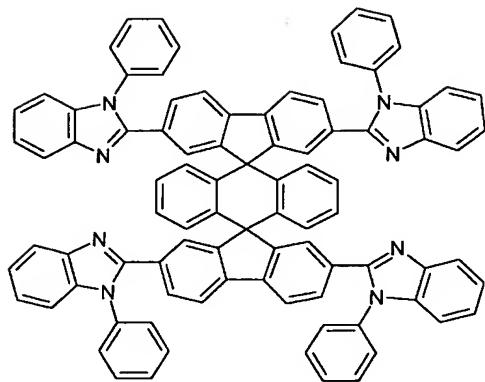


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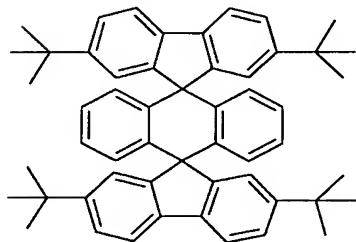
[Chemical Formula 18]



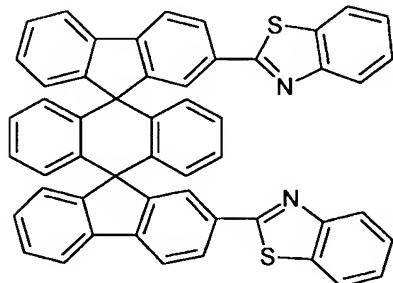
[Chemical Formula 19]



[Chemical Formula 20]

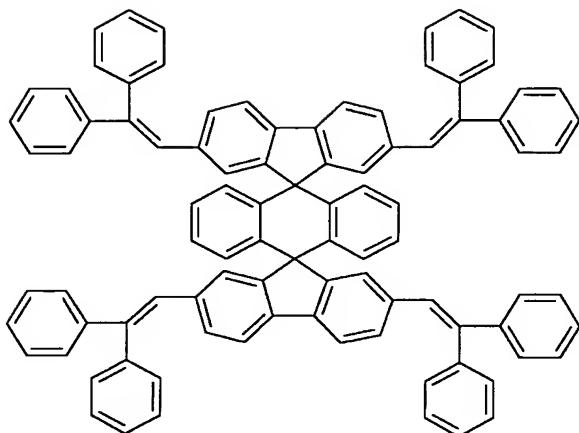


[Chemical Formula 21]



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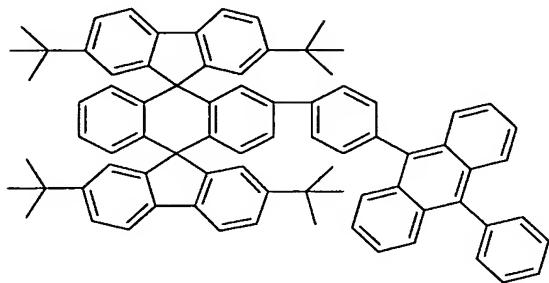
[Chemical Formula 22]



In structure of chemical formula 1a, phenyls of A, A', B and B' can be simultaneously substituted with mixing examples of substituents of A, A' and examples of substituents of B and B' such as compound of chemical formula 23.

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[Chemical Formula 23]



In structure of chemical formula 1a, polymer which is repetition of structure represented by chemical formula 1 can be synthesized by introducing adequate linking group into phenyls of B and B'.

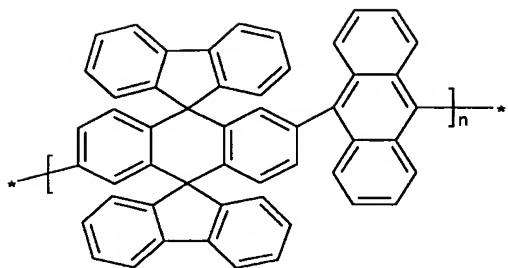
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The polymer is desirable to manufacture organic EL using spin-coating, roll-coating, screen-printing, ink-jet printing, not vaccum deposition. The major examples of the polymer are the following compounds of chemical formula 24 to 26.

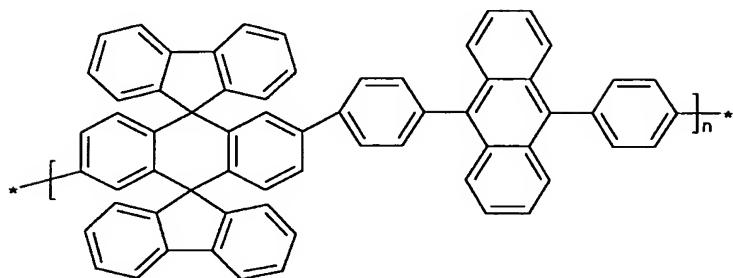
n represented by the following chemical formula 24 to 26 is integer of 2 or more.

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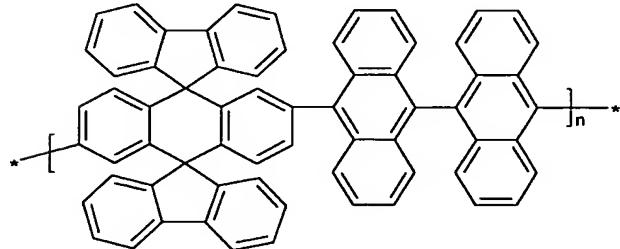
[Chemical Formula 24]



[Chemical Formula 25]



[Chemical Formula 26]



5

Examples of compounds satisfying chemical formula 1 is only for understanding the present invention, and the present invention is not limited by the compounds of examples.

Since compound contained in organic EL has high melting point and excellent sublimability, the compounds can be variously used as EL required high proton efficiency, EL required transporting an electron or a hole, organic solar cell comprising organic material, solar cell, optical photo conductor drum used in copier or laser printer, or organic transistor as well as application of organic EL.

The below examples will explain in more detail method for synthesizing compound represented by chemical formula 1 and manufacturing organic EL.

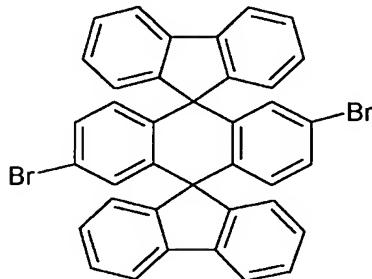
However, the present invention is not limited by the examples, and the examples are only for illustration.

### Examples of Synthesis

#### Preparative Example 1: Synthesis of Chemical Compound 27

To synthesize Chemical Compound 1, the below Chemical Compound 27 used as start material was synthesized as follows.

5 [Chemical Compound 27]



To a solution of 2-bromobiphenyl (5.0g, 21.5 mmol) in THF (50 ml) was added dropwise t-BuLi (32 ml of a 1.7 M solution in pentane) at -78 °C. After the mixture had been stirred for 1 hr at -78°C , 2,6-dibromoanthraquinone (3 g, 8.2 mmol) was added. The cooling bath was removed and the mixture was stirred for 30 min. And then the mixture was stirred for 4 hr at room temperature. The reaction mixture was poured into diethyl ether (30 ml) and 2 N HCl (50 ml), and stirred for 30 min at room temperature. The precipitate was filtered off with suction, washed with water and ethyl ether, and dried.

15 5.1 g of solid sample synthesized as above was suspended in acetic acid (60 ml), and HCl(35% aqueous solution, 5 drops) was added thereto. After the reaction mixture had been stirred while refluxing for about 15 hours, it was cooled to room temperature. The precipitate was filtered off with suction, washed with acetic acid, and then dried to obtain Chemical Compound 27 (4.6 g, 88%) as white solid.

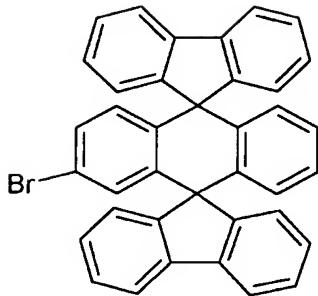
20 NMR analysis result of Chemical Compound 27 is as follows:

<sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) d 8.12 (4H, d), 7.52 (4H, t), 7.32 (4H, t), 7.06 (4H, d), 6.84 (2H, d), 6.28 (2H, s), 6.16 (2H, d)

#### Preparative Example 2: Synthesis of Chemical Compound 28

25 To synthesize Chemical Compound 1, the below Chemical Compound 28 used as start material was synthesized as follows.

[Chemical Compound 28]



To a solution of 2-bromobiphenyl (2.68 g, 11.5 mmol) in THF (35 ml) was added dropwise t-BuLi (16.9 ml of a 1.7 M solution in pentane) at -78 °C. After the mixture had been stirred for 40 min at -78 °C, 2-bromoanthraquinone (1.44 g, 5 mmol) was added. The cooling bath was removed and the mixture was stirred for 3 hours at room temperature. The reaction mixture was poured into diethyl ether (15 ml) and 2 N HCl (55 ml), and stirred for 30 min. The precipitate was filtered off with suction, washed with water and ethyl ether, and then dried.

2.5 g of solid sample synthesized as above was suspended in acetic acid (50 ml), and conc. H<sub>2</sub>SO<sub>4</sub>(10 drops) was added thereto. The reaction mixture had been stirred at reflux for about 3 hours, it was cooled to room temperature. The precipitate was filtered off with suction, washed with acetic acid, and then dried to Chemical Compound 28 (2.2 g, 79%) as white solid.

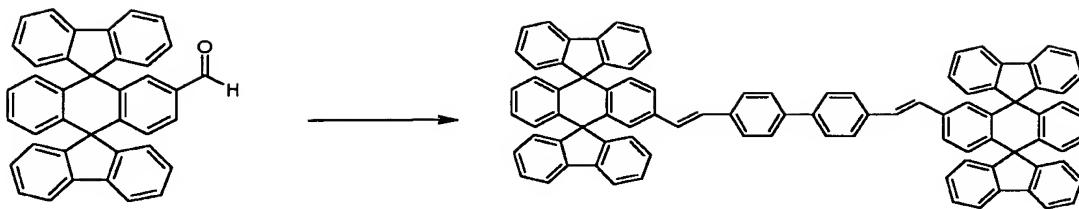
NMR analysis result of Chemical Compound 27 is as follows:  
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.9 (4H, m), 7.5-7.4 (4H, m), 7.3 (4H, t), 7.2 (4H, m), 6.9 (1H, d), 6.8 (2H, m), 6.5 (1H, s), 6.3 (2H, m), 6.2 (1H, d)

#### Example 1: Synthesis of Chemical Compound 16

To synthesize Chemical Compound 1, Chemical Compound 16 was synthesized using Chemical Compound 29 as start material as follows.

[Chemical Compound 29]

[Chemical Compound 16]



To a solution of Chemical Compound 29 (1.34 g, 2.6 mmol) and 4,4'-bis(diethylphosphorylmethyl)biphenyl (0.50 g, 1.3 mmol) in DMF (80 ml) was added dropwise lithium ethoxide (2.8 ml of a 1.0 M solution in ethanol) at room temperature under nitrogen. After the reaction mixture had been stirred at room temperature for 12 hours, it was filtered off with suction, washed with water, ethanol and dried under vacuum. Purification by sublimation afforded Chemical Compound 16 as white solid.

Analysis calculated for  $C_{90}H_{56}$ : C, 94.9; H, 5.02. Found: C, 94.4; H, 5.12;  
MS ( $M^+$ ) calculated for  $C_{90}H_{56}$  1162, found 1163.

Example 2: Synthesis of Chemical Compound 8

To synthesize Chemical Compound 1, Chemical Compound 8 was synthesized using Chemical Compound 27 as start material as follows.

Chemical Compound 27 (0.36 g, 0.75 mmol), 2,2'-diphenylvinyl-1-boronic acid, and tetrakis(triphenylphosphine)palladium (86 mg, 0.075 mmol) were slurried in a mixture of toluene (20 ml) and aqueous potassium carbonate solution (10 ml, 2 N). With vigorous stirring, the mixture was boiled under reflux for 24 hours. After cooling to room temperature, the organic layer was separated, washed with water, dried over  $MgSO_4$ , and concentrated under vacuum. Recrystallization from chloroform and ethanol afforded Chemical Compound 8 (75%) as white solid.

Analysis calculated for  $C_{66}H_{44}$ : C, 94.70; H, 5.30. Found: C, 94.30; H, 5.40;  
MS ( $M^+$ ) calculated for  $C_{66}H_{44}$  836, found 837;  
mp 387.7 °C

Example 3: Synthesis of Chemical Compound 15

To synthesize Chemical Compound 1, Chemical Compound 15 was synthesized using Chemical Compound 28 as start material as follows.

To a solution of Chemical Compound 28 (5.6 g, 10.0 mmol), in dry THF (60 ml) was added dropwise t-BuLi (17.6 ml of a 1.7 M solution in pentane) at -78 °C under nitrogen. After the mixture had been stirred for 1 hour, trimethylborate (4.5 ml) was added dropwise. The cooling bath was removed and the mixture was stirred for 3 hours at room temperature. The mixture was quenched with 1 N HCl (150 ml)

and stirred for 1.5 hour at room temperature. The precipitate was filtered with suction, washed with water and dried under vacuum.

To a suspension of 9,10-dibromoanthracene (60 mg), the obtained solid material (0.20 g), and potassium phosphate (0.16 g) in DMF (10 ml) was added 5 tetrakis(triphenylphosphine)palladium (12 mg). After the reaction mixture had been stirred at 60 °C for 18 hours, it was cooled to room temperature and ethanol (20 ml) was added. After addition, the reaction mixture was further stirred at room 10 temperature for 30 minutes. The precipitate was filtered off with suction. Then it was dissolved in N-methyl pyrrolidine (50 ml) and filtered through a short column packed with silica gel. After removal of solvent, the crude product was purified by crystallizing from ethanol to give Chemical Compound 15 (0.16 g, 41%).

Analysis calculated for  $C_{90}H_{54}$ : C, 95.21; H, 4.79. Found: C, 94.90; H, 4.70;  
MS (M+) calculated for  $C_{90}H_{54}$  1134, found 1135.

Example 4: Synthesis of Chemical Compound 10

To synthesize Chemical Compound 1, Chemical Compound 10 was synthesized using Chemical Compound 28 as start material as follows.

To a solution of Chemical Compound 28 (5.6 g, 10.0 mmol), in dry THF (60 ml) was added dropwise t-BuLi (17.6 ml of a 1.7 M solution in pentane) at -78 °C under nitrogen. After the mixture had been stirred for 1 hour, trimethylborate (4.5 ml) was added dropwise. The cooling bath was removed and the mixture was stirred 20 for 3 hours at room temperature. The mixture was quenched with 1 N HCl (150 ml) and stirred for 1.5 hour at room temperature. The precipitate was filtered with suction, washed with water and dried under vacuum.

To a suspension of 9-bromo-10-phenylanthracene (0.3 g), the obtained solid 25 materia (0.52 g), and potassium phosphate (0.42 g) in DMF (10 ml) was added tetrakis(triphenylphosphine)palladium (35 mg, 0.03 mmol) under nitrogen. After the reaction mixture had been stirred at 60 °C for 12 hours, it was cooled to room temperature. Ethanol (20 ml) was added to the mixture, and then the mixture was stirred for 30 minutes at room temperature. The precipitate was filtered off with 30 suction, and then it was dissolved in chloroform (150 ml) and filtered through a short column packed with silica gel. After removal of solvent, the crude product was purified by crystallizing from ethanol to give Chemical Compound 10 (0.26 g, 35%).

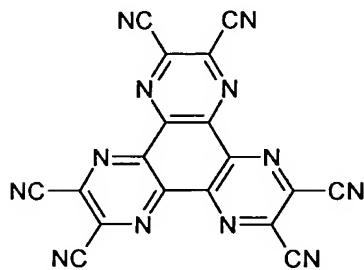
Analysis calculated for  $C_{90}H_{54}$ : C, 95.0; H, 4.95. Found: C, 94.9; H, 4.83;  
MS (M+) calculated for  $C_{58}H_{36}$  732, found 733.

## Examples of Organic EL Devices

### Comparative Example 1

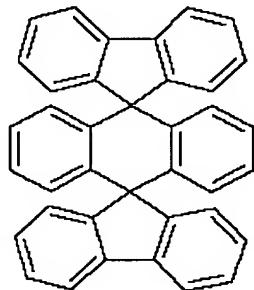
5 A glass substrate coated with a thin film of ITO (indium tin oxide) having thickness of about 1500 Å was ultrasonically cleaned in a solution of a cleaning agent, dried, and transferred into a plasma cleaning device. The substrate was cleaned with oxygen plasma for 5 minutes, and transferred to a thermal vapor deposition chamber. A hole-injecting layer having thickness of about 500 Å was formed by thermal vacuum deposition of the hexanitrile hexaazatriphenylene of Chemical Compound 30, a stable hole-injecting material, over the ITO (anode).

10 [Chemical Compound 30]



15 A hole-transporting layer having thickness of about 600 Å was formed by thermal vacuum deposition of NPB, a hole-transporting material, over the hole-injecting layer. An emitting layer having thickness of about 150 Å was formed by thermally vacuum depositing Chemical Compound 31 over the hole-transporting layer. On top of the light-emitting layer, 8-hydroxyquinoline Aluminum salt (Alq3), an n-type organic semiconductor, was deposited with thickness of about 300 Å to form an electron-transporting layer.

20 [Chemical Compound 31]



Then, a cathode electrode was formed by depositing 5 Å of LiF and about 2500 Å of aluminum on the electron-transporting layer. In the process, the

deposition speed was controlled to maintain 1 Å/sec for organic material, 0.2 Å/sec for lithium fluoride, and 3-7 Å/sec for aluminum.

When forward bias of 10.1 V was applied across the light-emitting device, blue light emission of 57 nit corresponding to x=0.218, y=0.301 was observed on basis of 1931 CIE color coordinate at a current density of 10 mA/cm<sup>2</sup>.

Example 5

A glass substrate coated with a thin film of ITO (indium tin oxide) having thickness of about 1500 Å was ultrasonically cleaned in a solution of a cleaning agent, dried, and transferred into a plasma cleaning device. The substrate was cleaned with oxygen plasma for 5 minutes, and transferred to a thermal vapor deposition chamber.

A hole-injecting layer having thickness of about 500Å was formed by thermal vacuum deposition of copper phthalocyanine over the ITO (anode). A hole-transporting layer having thickness of about 600Å was formed by thermal vacuum deposition of NPB, a hole-transporting material, over the hole-injecting layer. An emitting layer having thickness of about 400Å was formed by thermally vacuum depositing Chemical Compound 16 over the hole-transporting layer. On top of the light-emitting layer, 8-hydroxyquinoline Aluminum salt (Alq3), an n-type organic semiconductor, was deposited with thickness of about 200 Å to form an electron-transporting layer.

Then, a cathode electrode was formed by depositing 5 Å of LiF and about 2500 Å of aluminum on the electron-transporting layer. In the process, the deposition speed was controlled to maintain 1 Å/sec for organic material, 0.2 Å/sec for lithium fluoride, and 3-7 Å/sec for aluminum.

When forward bias of 9.1 V was applied across the light-emitting device, blue light emission of 126 nit corresponding to x=0.159, y=0.089 was observed on basis of 1931 CIE color coordinate at a current density of 10 mA/cm<sup>2</sup>.

Example 6

A glass substrate coated with a thin film of ITO (indium tin oxide) having thickness of about 1500 Å was ultrasonically cleaned in a solution of a cleaning agent, dried, and transferred into a plasma cleaning device. The substrate was cleaned with oxygen plasma for 5 minutes, and transferred to a thermal vapor deposition chamber.

A hole-injecting layer having thickness of about 500Å was formed by thermal vacuum deposition of HNHATA of Chemical Compound 30 over the ITO

(anode). A hole-transporting layer having thickness of about 400Å was formed by thermal vacuum deposition of NPB, a hole-transporting material, over the hole-injecting layer. An emitting layer having thickness of about 300Å was formed by thermally vacuum depositing Chemical Compound 15 over the hole-transporting layer. On top of the light-emitting layer, 8-hydroxyquinoline Aluminum salt (Alq3), an n-type organic semiconductor, was deposited with thickness of about 300 Å to form an electron-transporting layer.

Then, a cathode electrode was formed by depositing 5 Å of LiF and about 2500 Å of aluminum on the electron-transporting layer. In the process, the deposition speed was controlled to maintain 1 Å/sec for organic material, 0.2 Å/sec for lithium fluoride, and 3-7 Å/sec for aluminum.

When forward bias of 6.6 V was applied across the light-emitting device, blue light emission of 254 nit corresponding to x=0.184, y=0.242 was observed on basis of 1931 CIE color coordinate at a current density of 10 mA/cm<sup>2</sup>.

Example 7

A glass substrate coated with a thin film of ITO (indium tin oxide) having thickness of about 1500 Å was ultrasonically cleaned in a solution of a cleaning agent, dried, and transferred into a plasma cleaning device. The substrate was cleaned with oxygen plasma for 5 minutes, and transferred to a thermal vapor deposition chamber.

A hole-injecting layer having thickness of about 500Å was formed by thermal vacuum deposition of HNHATA of Chemical Compound 30 over the ITO (anode). A hole-transporting layer having thickness of about 400Å was formed by thermal vacuum deposition of NPB, a hole-transporting material, over the hole-injecting layer. An emitting layer having thickness of about 200Å was formed by thermally vacuum depositing Chemical Compound 10 over the hole-transporting layer. On top of the light-emitting layer, 8-hydroxyquinoline Aluminum salt (Alq3), an n-type organic semiconductor, was deposited with thickness of about 300 Å to form an electron-transporting layer.

Then, a cathode electrode was formed by depositing 5 Å of LiF and about 2500 Å of aluminum on the electron-transporting layer. In the process, the deposition speed was controlled to maintain 1 Å/sec for organic material, 0.2 Å/sec for lithium fluoride, and 3-7 Å/sec for aluminum.

When forward bias of 6.7 V was applied across the light-emitting device, blue light emission of 168 nit corresponding to  $x=0.172$ ,  $y=0.156$  was observed on basis of 1931 CIE color coordinate at a current density of  $10 \text{ mA/cm}^2$ .

Example 8

5 A glass substrate coated with a thin film of ITO (indium tin oxide) having thickness of about  $1500 \text{ \AA}$  was ultrasonically cleaned in a solution of a cleaning agent, dried, and transferred into a plasma cleaning device. The substrate was cleaned with oxygen plasma for 5 minutes, and transferred to a thermal vapor deposition chamber.

10 A hole-injecting layer having thickness of about  $500 \text{ \AA}$  was formed by thermal vacuum deposition of HNHATA of Chemical Compound 30 over the ITO (anode). A hole-transporting layer having thickness of about  $400 \text{ \AA}$  was formed by thermal vacuum deposition of Chemical Compound 10, a hole-transporting material, over the hole-injecting layer. On top of the light-emitting layer, 8-hydroxyquinoline 15 Aluminum salt ( $\text{Alq}_3$ ), an n-type organic semiconductor, was deposited with thickness of about  $300 \text{ \AA}$  to form an electron-transporting layer.

20 Then, a cathode electrode was formed by depositing  $5 \text{ \AA}$  of LiF and about  $2500 \text{ \AA}$  of aluminum on the electron-transporting layer. In the process, the deposition speed was controlled to maintain  $1 \text{ \AA/sec}$  for organic material,  $0.2 \text{ \AA/sec}$  for lithium fluoride, and  $3-7 \text{ \AA/sec}$  for aluminum.

When forward bias of 7.8 V was applied across the light-emitting device, blue light emission of 464 nit corresponding to  $x=0.326$ ,  $y=0.550$  was observed on basis of 1931 CIE color coordinate at a current density of  $10 \text{ mA/cm}^2$ .

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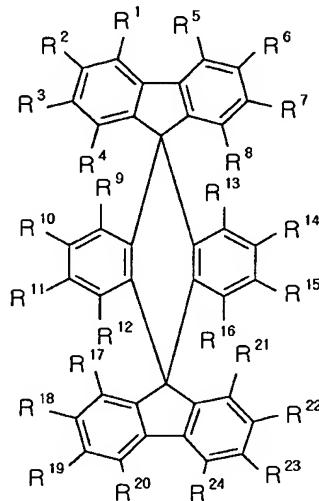
Advantageous Effect

30 Double-spiro organic compounds according to the present invention have high melting point and provide fluorescent dopant properties used in light-emitting, hole-transporting, electron-transporting properties and characteristics, which are favorable in the organic EL devices. Therefore, when used in preparing organic EL devices, double-spiro organic compounds of the present invention improve driving life and thermal stability to the organic EL devices.

WHAT IS CLAIMED IS:

1. A double-spiro compound of Chemical Formula 1:

[Chemical Formula 1]



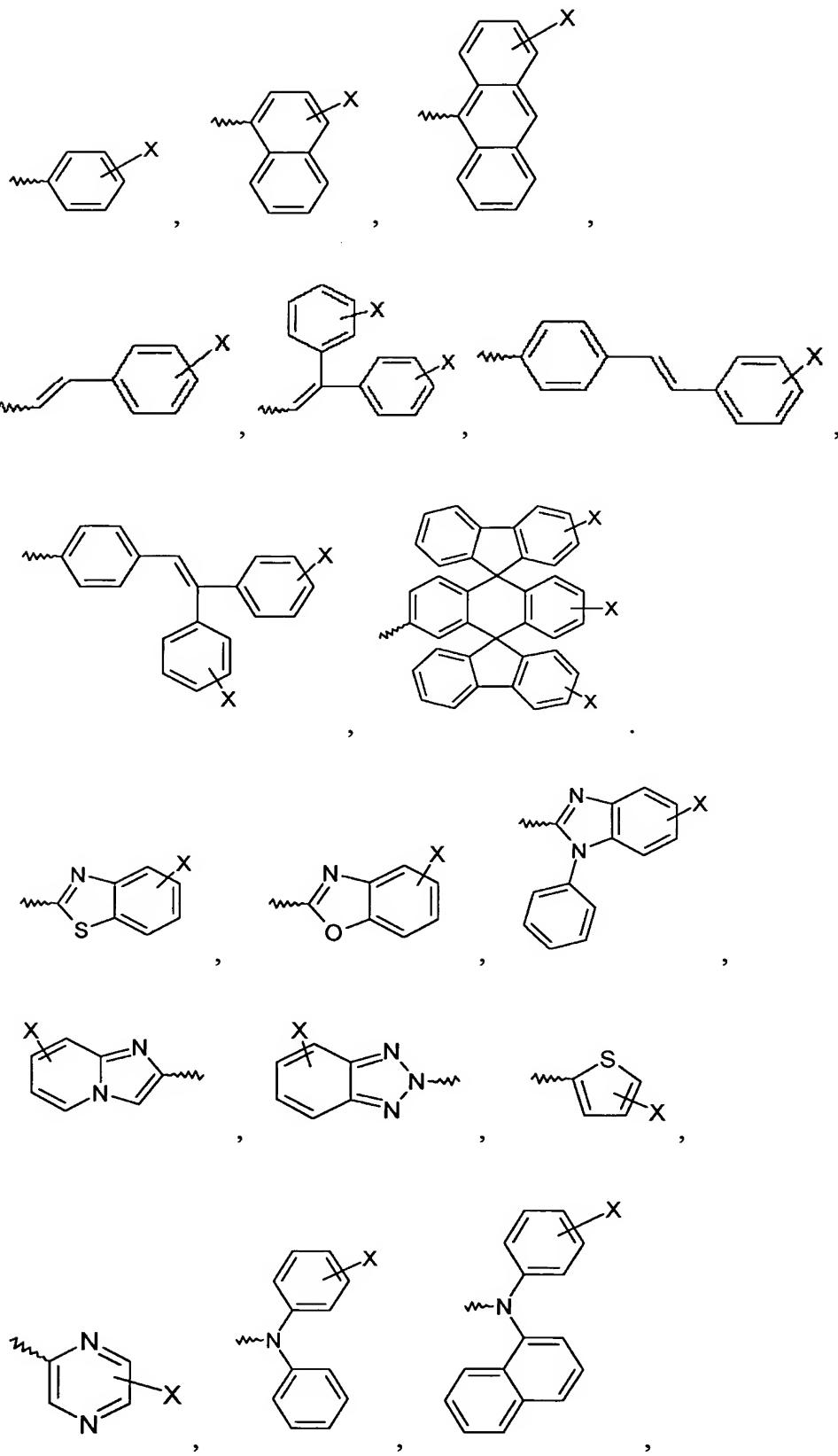
5 wherein each of R1-R24 is, independently or simultaneously, hydrogen; a halogen group selected from the group consisting of fluorine(F), chlorine(Cl), bromine(Br), and iodine(I); an aliphatic hydrocarbon of C1-C20, alkoxy group, arylamine group; aromatic hydrocarbon; nitrile(-CN); acetylene group; a heterocyclic compound selected from the group consisting of thiazole, oxazole, imidazole, and thiophene; or a substituent which is moiety of compound represented by formula 1, which are unsubstituted or substituted with at least one of substituent X defined as follows,

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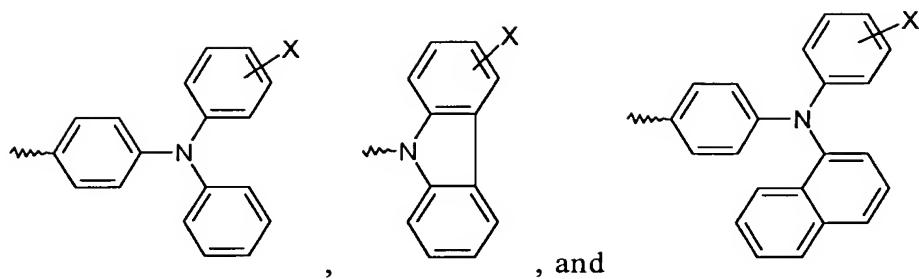
R10 and 11, and R14 and R15 are independently or simultaneously combined to aromatic ring or heterocycle,

15 the substituent X is hydrogen, halogen group of fluorine, chlorine, bromine, or iodine; aliphatic hydrocarbon of C1-C20, alkoxy group, arylamine group; aromatic hydrocarbon; nitrile(-CN); acetylene group; heterocyclic compound selected from the group consisting of thiazole, oxazole, imidazole, and thiophene; or a substituent which is moiety of compound represented by formula 1, which are 20 unsubstituted or substituted with at least one of substituent X.

2. The double-spiro compound of Claim 1, wherein one or more of R1-R24 are selected from the following substituent groups:



5

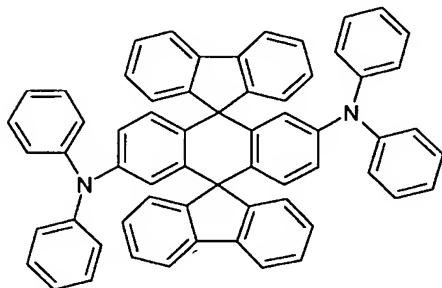


wherein X is hydrogen, halogen group of fluorine, chlorine, bromine, or iodine; aliphatic hydrocarbon of C1-C20, alkoxy group, arylamine group; aromatic hydrocarbon; heterocyclic compound selected from the group consisting of thiazole, 5 oxazole and imidazole; nitrile(-CN); acetylene group; or a substituent which is moiety of compound represented by formula 1,

and X may form fused ring to be fused with heterocyclic ring of original substituents of Compound Formula I.

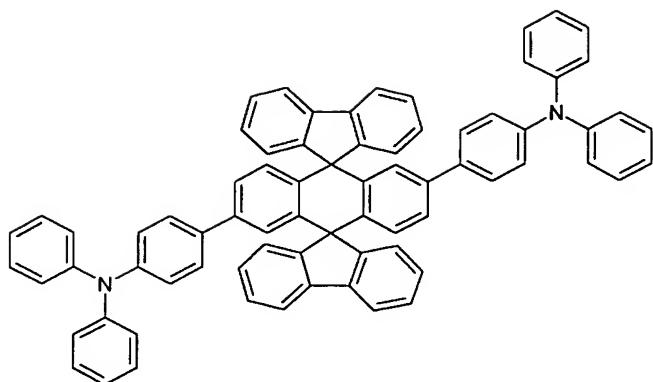
3. The double-spiro compound of Claim 1, wherein the compound is 10 represented by Chemical Formula 2 below.

[Chemical Formula 2]



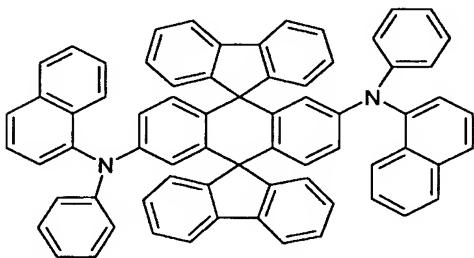
4. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 3 below.

15 [Chemical Formula 3]



5. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 5 below.

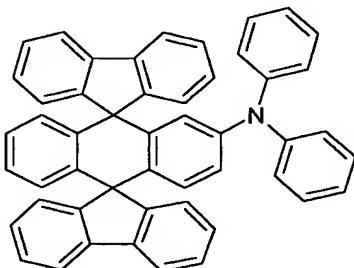
[Chemical Formula 4]



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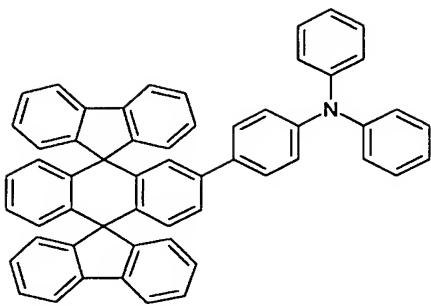
6. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 5 below.

[Chemical Formula 5]



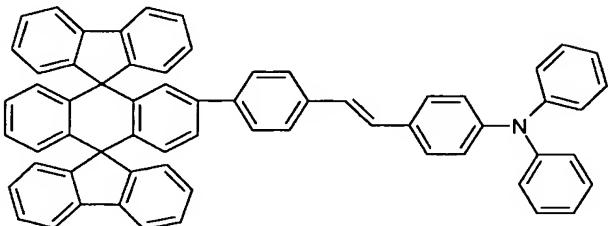
10 7. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 6 below.

[Chemical Formula 6]



8. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 7 below.

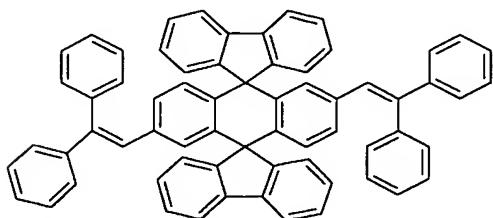
[Chemical Formula 7]



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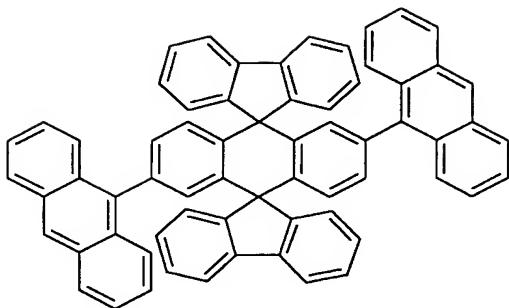
9. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 8 below.

[Chemical Formula 8]



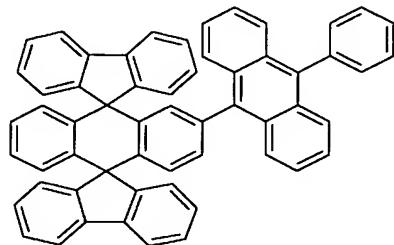
10. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 9 below.

[Chemical Formula 9]



11. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 10 below.

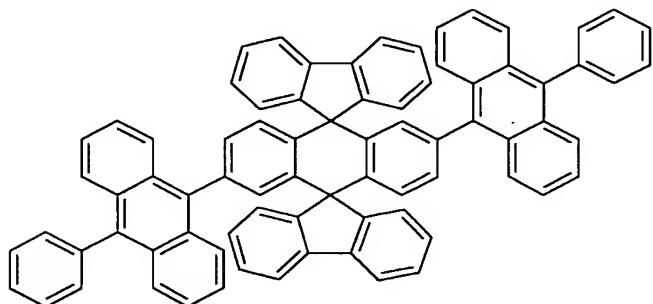
[Chemical Formula 10]



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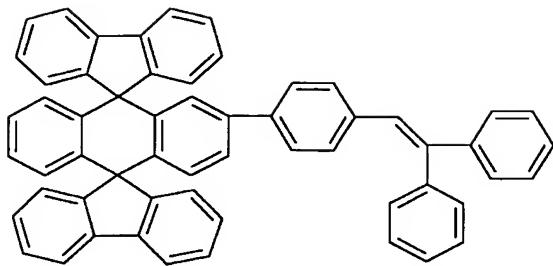
12. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 11 below.

[Chemical Formula 11]



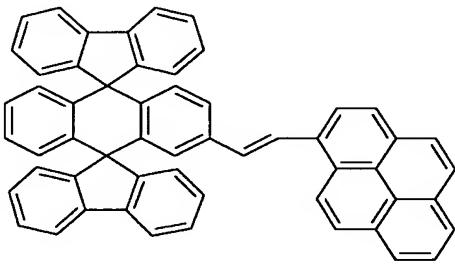
10 13. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 12 below.

[Chemical Formula 12]



14. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 13 below.

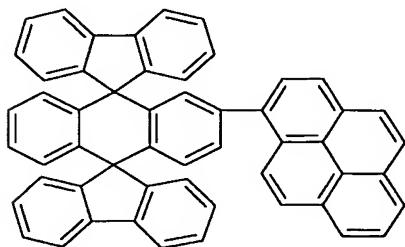
[Chemical Formula 13]



5

15. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 14 below.

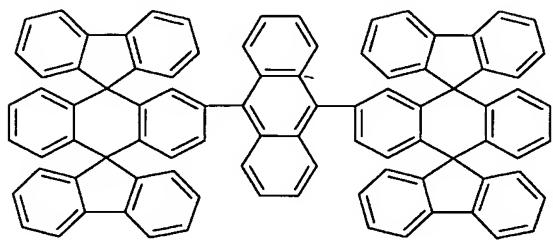
[Chemical Formula 14]



10

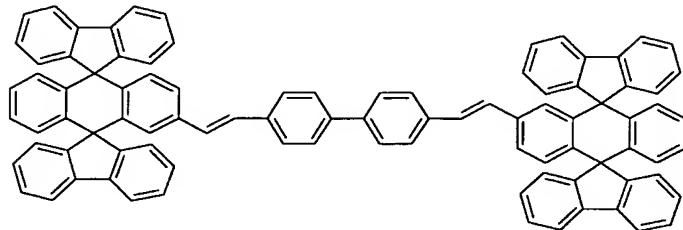
16. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 15 below.

[Chemical Formula 15]



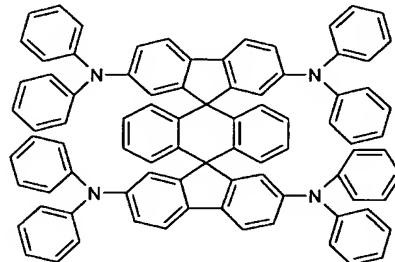
17. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 16 below.

[Chemical Formula 16]



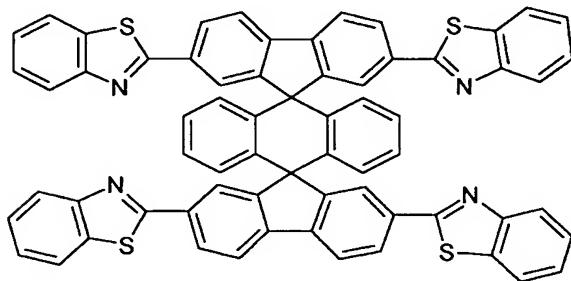
5 18. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 17 below.

[Chemical Formula 17]



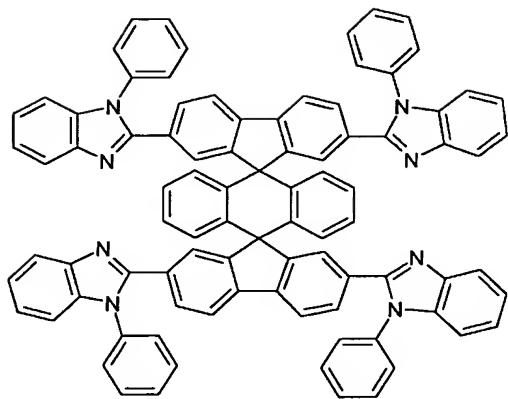
10 19. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 18 below.

[Chemical Formula 18]



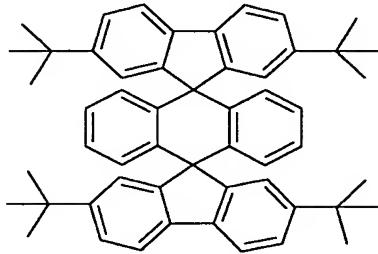
20. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 19 below.

15 [Chemical Formula 19]



21. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 20 below.

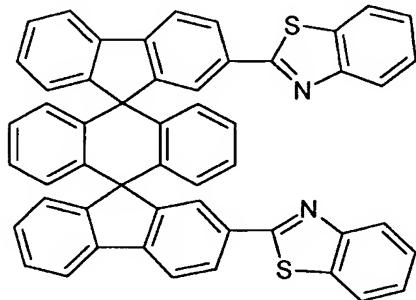
[Chemical Formula 20]



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22. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 21 below.

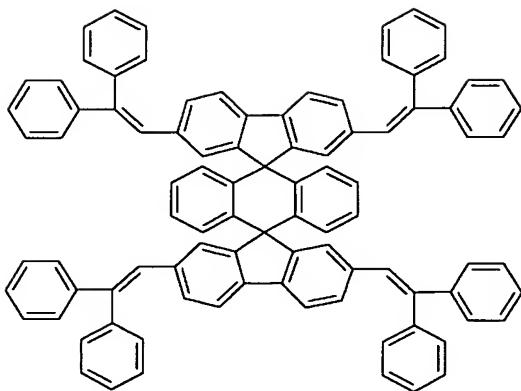
[Chemical Formula 21]



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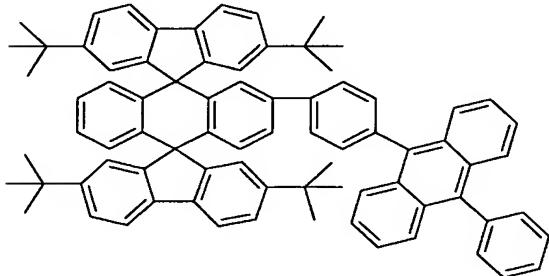
23. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 22 below.

[Chemical Formula 22]



24. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 23 below.

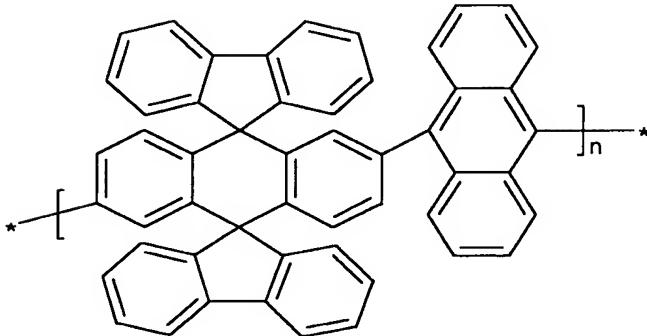
[Chemical Formula 23]



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25. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 24 below.

[Chemical Formula 24]

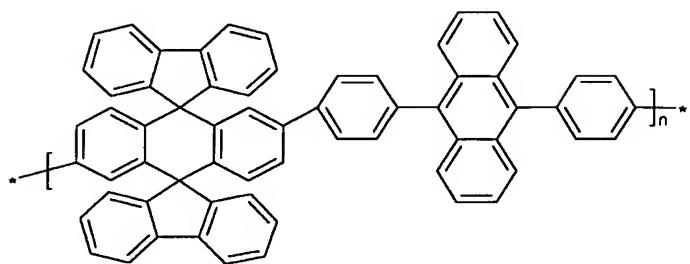


10

wherein n is an integer of two or more.

26. The double-spiro compound of Claim 1, wherein the compound is represented by Chemical Formula 25 below.

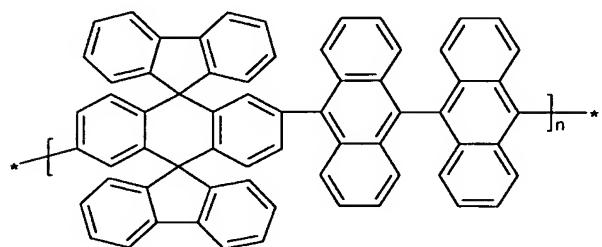
### [Chemical Formula 25]



wherein  $n$  is an integer of two or more.

27. The double-spiro compound of Claim 1, wherein the compound is  
5 represented by Chemical Formula 26 below.

### [Chemical Formula 26]

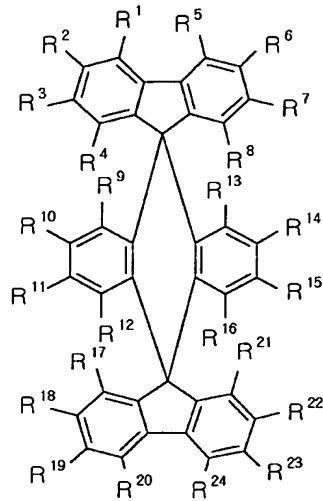


wherein  $n$  is an integer of two or more.

Abstract of the Disclosure

The present invention provides a double spiro type of organic compound which has high melting point and high quantum efficiency, and can control mobility of carrier. The double spiro compound has structure improving hole-transporting, 5 light-emitting, fluorescent dye, and electron-transporting properties.

For this, the present invention provides a double spiro compound represented by Chemical Formula 1:



Chemical Formula 1

10 The double-spiro organic compounds according to the present invention have high melting point and provide fluorescent dopant properties used in light-emitting, hole-transporting, electron-transporting properties and characteristics, which are favorable in the organic EL devices. Therefore, when used in preparing organic EL devices, double-spiro organic compounds of the present invention improve driving 15 durability and thermal stability to the organic EL devices.



Figure 1

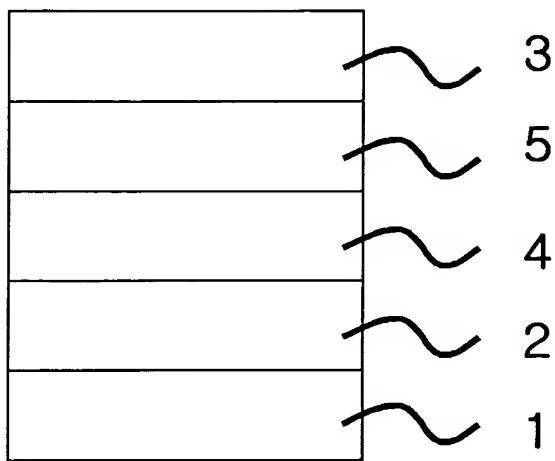


Figure 2

